

## RESIDUES OF ORGANOCHLORINE PESTICIDES IN THE TOPSOILS OF HARBIN, CHINA

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### Abstract:

Topsoil samples were collected in and around Harbin, a city in, northeast of China, to assess concentration level of organochlorine pesticides (OCPs) in soil. The mean concentrations (in pg/g dry weight (dw)) were 10700 for HCH, 6840 for DDT, 6.6 for chlordane, and 3.4 for endosulfan, respectively, indicating that HCH and DDT were the dominant OCPs detected in soil samples.  $\beta$ -HCH predominated the HCH compositions in the studied soils, which confirmed that the residues of HCH were from past usage technical HCH. DDTs residues in the study region were probably from historical application. The concentration of chlordane and endosulfan were quite low and ratio of isomers indicating that were from past usage or transformed by atmospheric long-rang transport (ALRT).

### 1. Introduction

Organochlorine pesticides (OCPs) are toxic, bioaccumulative and are able to transport for a long distance. OCPs have been used in China for a long time, but most of studies on residues in soil sample concentrated on DDT and HCH only<sup>1-4</sup>, and others, such as endosulfan and chlordane, were seldom reported due to low concentration below the detection limit.

Harbin, located in northeastern China, is the capital of Heilongjiang Province. Harbin is a major commercial, industrial, and transportation center, which is situated in a productive farming region. The population in 2000 was estimate to be almost 3million. The annual average temperature in Harbin was 3.6°C, the minimum mean in January was -13.2~-24.8 °C, and the average high in July was 18.1~22.8 °C. There was little information on OCPs residues in Harbin region. The object of our study is to investigate the current status of OCP residues in Harbin, included HCH, DDT, endosulfan and chlordane.

### 2. Materials and methods

Details of collect, process, and analysis of samples are reported elsewhere<sup>5</sup>. Sixteen topsoil samples (0-20cm) were collected in Harbin region in October, 2006. The samples were collected using a stainless steel scoop pre-washed with acetone, placed in a pre-washed glass flask with teflon cap, and kept frozen in the laboratory of the International Joint Research Center for Persistent Toxic Substances (IJRC-PTS), Harbin Institute of Technology, Harbin, where they were stored frozen (-20°C) before extraction. About 20 grams of soil were Soxhlet extracted for 24h with 100 ml mix solvent (n-hexane/acetone, 1:1 v/v). The extract was filtered through a funnel filled with anhydrous sodium sulfate then rotary-evaporated to 4 ml. The extract was passed through 10 g silica gel column, eluted with 50ml mixture of hexane and dichloromethane (DCM, 1:1, v/v). The elution was rotary-evaporated to 2 ml and then reduced to 1 ml under a gentler nitrogen gas flow.

Analysis by GC-ECNI-MS was performed on an Agilent 6890GC-5975B MS detector with a HP-5MS capillary column (30m×0.25mm i.d., 0.25 $\mu$ m film thickness), operating on single ion monitoring (SIM) mode. Helium was used as the carrier gas with methane as reaction gas. GC oven program was 80°C for 1min, 10°C/min to 160°C, 2°C/min to 250°C, 30°C/min to 300°C. Injections (2 $\mu$ L) were splitless with split opened after 1.0min, injector and transfer line temperatures were 250°C and 300°C, respectively. The soil organic carbon (SOC) for each sample was measured by using a Shimadzu TOC Analyzer (Model TDC-VCPN, Kyoto, Japan). The lower limit for quantitative analysis was 50 pg/mL for  $\alpha$ -HCH, 550 pg/mL for  $\beta$ -HCH, 30 pg/mL for  $\gamma$ -HCH, 20 pg/mL for chlordane, endo 1 and endo 2, 300 pg/mL for p,p'-DDE, 800 pg/mL for p,p'-DDD, 450 pg/mL for

o,p'-DDT, 3500 pg/mL for p,p'-DDT. Replicate analyses were performed on site 7. The relative standard deviations (RDS) were ranged 2.59-13.90% for HCH, 0.05-0.11% for chlordane, 6.06-15.19% for all DDT metabolizes except for p,p'-DDT (123.94%). To check method recoveries, two spike samples were prepared by adding 100  $\mu$ L of the standard pesticide mix (60ng). Average recoveries ranged from 74.8-101.7%. Blank were run by soxhlet extracting a thimble filled with sodium sulfate and treating the extract as a sample. Blank values for all the other compound were below the quantification limits expect for  $\gamma$ -HCH (40 pg/mL) which below 5.1% of the soil sample. All the sample results were reported without blank correction.

### 3 Result and discussion

#### 3.1. HCH and DDT

Figure 1 presents the concentrations of  $\Sigma$ HCH ( $\alpha$ -HCH +  $\beta$ -HCH +  $\gamma$ -HCH) and  $\Sigma$ DDT (p,p'- DDT+ o,p'- DDT+ o,p'- DDE+ o,p'- DDD). Concentrations of  $\Sigma$ HCH ranged from 260 pg/g to 51,760 pg/g dw (dry weight) with a mean concentration of 10,700 pg/g dw. The highest concentrations occurred at Site 12 (vegetable land) followed by Site 9 (garden) and Site 13 (vegetable land), it is because that vegetable lands and gardens in China usually use more pesticides than other soils<sup>5</sup>. The mean concentrations of HCH isomers in the investigated soils sample from Harbin area were as follows:  $\beta$ : $\alpha$ : $\gamma$  = 34:3:1, indicating that the technical HCH had not been in use in the Harbin area for a long time. The ratios of  $\alpha$ -HCH/ $\gamma$ -HCH were between 2 and 4, means very little use of lindane (pure  $\gamma$ -HCH) in this region. Therefore HCH source in Harbin region was from historical local technical HCH contamination, rather than current input.

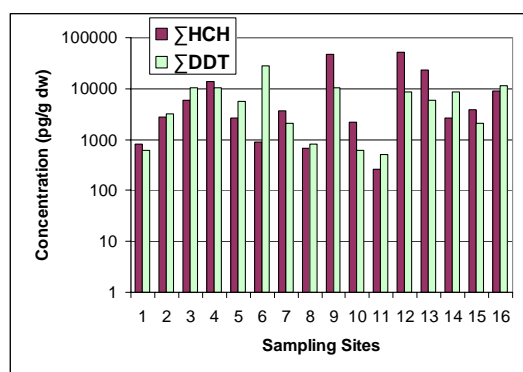


Figure 1. Concentrations of  $\Sigma$ HCH and  $\Sigma$ DDT in topsoil (sampling sites: 1-5, grassland; 6-8, woodland; 9, garden; 10, playground; 11, industry; 12-16, vegetable land.)

for technical DDT/DDE, average ratio was 3.49 this indicated that DDE was probably from historical application on Harbin area.

In comparison to other cities in China, the average ratio of 3.5 for p,p'-DDT/p,p'-DDE in topsoil in Harbin is higher than Beijing (mean 2.0)<sup>1</sup>, Tianjin (<1)<sup>2</sup> and Guangzhou (2)<sup>3</sup>. Possible explanations are that DDT is more persistent in Harbin soils because of much lower temperature in the city.

The ratio of p,p'-DDT/o,p'-DDT also could be as another approach to provide further information about whether it was being currently applied or residue from past application. However, in our present study, the average values for p,p'-DDT/o,p'-DDT was 7 (range 1.38-12.17) which were similar to Alabama (ratio:6), USA soils<sup>8</sup>, but were little higher than technical DDT( ratio:5). It has been explained that p,p'-DDT and o,p'-DDT have declined at similar rates since application ceased in Alabama<sup>8</sup>. So DDTs residues in the study region were probably from historical application and degraded at different dissipation rates for DDT isomers. Comparison of the HCH and DDT level in Harbin soil samples with other locations of China found that DDT residues (6,840 pg/g) were lower than Beijing (140,000 pg/g), Guangzhou (133,500 pg/g) and HCH residues (10,700 pg/g dw)

As shown in Figure 1, the content of  $\Sigma$ DDT ranged from 520 to 28,000 pg/g dw (mean 6840 pg/g dw). The highest concentration was in Site 6 and the lowest concentration was in site 11. As we known, technical DDT typically contains 77.1% p,p'-DDT, 14.9% o,p'-DDT, 4% p,p'-DDE. DDT can be transformed to DDE under aerobic condition while to DDD under anaerobic condition. The ratio of DDT/DDE have been used to infer sources and qualitatively judge the age of contaminant residues in soil. In general, a small value of DDT/DDE ratio is indicative of aged DDT, but Ricardo<sup>6</sup> gave another evidence that the process of degradation from DDT to DDE was very slow in soil and volatilization was the main process responsible for the DDT dissipation. It was indicated that DDT persists with a half-life of 20-30 years. The ratio of DDT/DDE ranged from 13 to 1.3 after twenty-five years because of slowly metabolism of DDT<sup>7</sup>. The ratio for the study 16 soil samples ranged from 0.88 (site 6/woodland) to 7.58 (site 14/vegetable) were lower than the ratio 19.27

were higher than Guangzhou (4,390 pg/g), and similar to Beijing (10,360 pg/g).

### 3.2 Chlordane and Endosulfan

Concentration of both chlordane and endosulfan in topsoil from Harbin were low, as shown in Figure 2. Concentrations of  $\sum$ chlordane (TC+CC+TN) ranged from 0.9 to 18.3 pg/g dw (mean: 6.6 pg/g dw) were lower than those from Lake Tai in China (40 pg/g)<sup>9</sup> and in archived soils in UK (range from <90 to 1,600 pg/g dw)<sup>10</sup> Average concentrations of total endosulfan were 3.2 pg/g dw (ranged from BDL(below detection limit) to 7.1 pg/g dw). These concentrations were very low as compared to those reported from other studies, such as in Argentina (mean concentration 16,500 pg/g dw)<sup>11</sup> where agrochemicals have never been used, and in Brazil (mean 500 pg/g dw)<sup>12</sup>

Technical chlordane is a mixture of components including *trans*-chlordane (TC), *cis*-chlordane (CC), *trans*-nonachlor (TN) and *cis*-nonachlor (CC) in the proportion of 1.00/0.77/0.62/0.15, respectively. Mean TC/CC/TN ratios were 1/1.38/2.38 in this study indicating that chlordane found in Harbin topsoil originated from past usage technical chlordane because of degradation rate in the order of TC>CC>TN. General use of chlordane in agriculture was banned in China in 1982. However, chlordane production has been resumed since 1988, and around 1,480 t of chlordane used has been for protection of constructions and dams from termites mainly in the south of China. To our knowledge, there were no records of past usage of chlordane in the north-east of China, the trend probably reflect background soil concentrations influenced by long-ranged atmospheric transport.

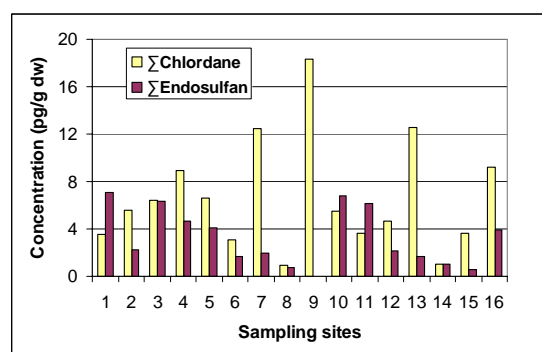


Figure 2. Concentrations of  $\sum$ chlordane and  $\sum$ endosulfan in topsoil from Harbin.

Technical endosulfan is a mixture of two isomers, that is endosulfan 1 and endosulfan 2, in the ratio of 7:3. Endosulfan in soil is degraded to the highly toxic endosulfan sulfate. Our results showed that endosulfan sulfate level in Harbin topsoil were almost equal or higher than its parent compounds (endosulfan 1 or endosulfan 2) in most of soil samples indicating weathered characteristics of the chemicals in soil. Around 25,700 t of endosulfan were used in China between 1994 and 2004, and major use of endosulfan was on cotton, and a small amount was used on wheat, tea, apple tree, and tobacco<sup>13</sup>. The use of endosulfan in Heilongjiang province was very low, therefore so were the concentrations of endosulfan in Harbin topsoil.

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